

SYNTHESIS OF BORON NITRIDE NANOTUBES FOR ENGINEERING APPLICATIONS

Janet Hurst
David Hull
NASA Glenn Research Center
21000 Brookpark Rd
Cleveland, Ohio 44135

Daniel Gorican
QSS Group
21000 Brookpark Rd
Cleveland, Ohio 44135

ABSTRACT

Boron nitride nanotubes (BNNT) are of significant interest to the scientific and technical communities for many of the same reasons that carbon nanotubes (CNT) have attracted wide attention. Both materials have potentially unique and important properties for structural and electronic applications. However of even more consequence than their similarities may be the complementary differences between carbon and boron nitride nanotubes. While BNNT possess a very high modulus similar to CNT, they also possess superior chemical and thermal stability. Additionally, BNNT have more uniform electronic properties, with a uniform band gap of 5.5 eV while CNT vary from semi-conductive to highly conductive behavior.

Boron nitride nanotubes have been synthesized both in the literature and at NASA Glenn Research Center, by a variety of methods such as chemical vapor deposition, arc discharge and reactive milling. Consistent large scale production of a reliable product has proven difficult. Progress in the reproducible synthesis of 1-2 gram sized batches of boron nitride nanotubes will be discussed as well as potential uses for this unique material.

INTRODUCTION

In the last decade, significant attention from the scientific community has been focused on the area of nanotechnology and specifically upon nanotube synthesis. While carbon nanotubes have generated the bulk of interest to date, other compositions offer promise as well and may have advantages or complementary properties relative to carbon nanotubes for various applications. At NASA Glenn Research Center, where application interests are often focused on high temperature propulsion, both BN and SiC nanotube synthesis are currently under investigation for high temperature structural and electronic materials (1,2). The focus of the current effort is BNNT synthesis. While boron nitride nanotubes are known to be structurally similar to carbon nanotubes, inasmuch as both are formed from graphene sheets, much less is known about BNNT. In large part this is due to the difficulty in synthesizing this material rather than lack of interest. It has been found that BNNT have excellent mechanical properties with a measured Young's modulus of 1.22 +/- 0.24 TPa (3). BNNT also have a constant band gap of about 5.5 eV (4). In contrast,

This is a preprint or reprint of a paper intended for presentation at a conference. Because changes may be made before formal publication, this is made available with the understanding that it will not be cited or reproduced without the permission of the author.

CNT vary from semi-conducting to conducting behavior depending on chirality and diameter of the product. Little progress has been demonstrated in the control of the chiral angle and hence the electronic properties of CNT. On the other hand, BNNT preferentially forms the zig-zag structure rather than the armchair or chiral structures due to the polar nature of the B-N bond (5). Recently, it has also been shown that BNNT systems have excellent piezoelectric properties, superior to those of piezoelectric polymers (6). Additionally, the expected oxidation resistance of BNNT relative to CNT suggests BNNT may be suitable for high temperature structural applications. This stability may be an important safety consideration for some applications, such as hydrogen storage, as carbon nanotubes readily burn in air. Many synthesis approaches have been tried with varying degrees of success. Among these approaches are pyrolysis over Co (7), CVD methods (8), arc discharge (9) laser ablation (10), and reactive milling techniques (11,12). The reported approach developed at NASA Glenn Research Center produced BNNT of significant length and abundance.

EXPERIMENTAL PROCEDURE

BNNT were prepared by reacting amorphous boron powder in a flowing atmosphere of nitrogen with a small amount of NH_3 . Prior to heat treatment, fine iron catalyst particles were added in the range of up to several weight percent and briefly milled in polyethylene bottles with a hydrocarbon solvent and ceramic grinding media. Batch sizes of 2 grams are typically produced but the process should be easily scaleable to larger sizes. Milled material was applied to various high temperature substrates such as alumina, silicon carbide, platinum and molybdenum. Nanotubes were formed during heat treatments to temperatures ranging from 1100 C to 1400 C for brief times, 20 minutes to 2 hours.

Nanotubes were imaged with a Hitachi S4700 field emission scanning electron microscope with a super thin window EDAX Genesis System energy dispersive spectrometer (EDS) or Phillips CM200 transmission electron microscope operated at 200 kV, with Gatan electron energy loss spectrometer (EELS). Thermogravimetric analysis (TGA) was done in air up to 1000 C.

RESULTS

BNNT synthesized by this method are shown in Figure 1. The low magnification photo in Figure 1a shows an as-produced flake of BNNT. The flake was removed by tweezers from a 2.5 mm x 5 mm substrate or crucible. It is robust and easily handled in this form. Also, as the nanotubes are anchored within a growth media, there is no respiration hazard. BN nanotubes grow extensively both from the "top" and "bottom" of the growth media, where "top" refers to the side exposed to the atmosphere. Both top and bottom layers can be observed in Figure 1a as the edges were slightly rolled during handling. The nanotubes are quite long, 100 microns being common as shown in Figures 1b and 1c. On the bottom of the growth media, a layer of shorter nanotubes develops between the film and substrate or crucible. EDS also showed that the BNNT grow upon a film composed primarily of B, N, O, Fe and some purities. Nanotube diameters can be very

consistent throughout their length; however this is processing temperature dependent. Not surprisingly, variation in the heat treatment temperature resulted in somewhat different product. Lower processing temperature, resulted in more fine, uniform nanotubes, as those shown in figure 1b. Diameters of 20nm to 50 nm were typical. Higher temperatures and/or longer times resulted in large “nanotube” growth as shown in Figure 2b. Growth originated from fine nuclei but with excessive temperature, large structures quickly developed, up to a few microns in diameter. As shown in Figures 2a and 2b, secondary nucleation of small diameter BNNT also occurred on these larger structures. Higher processing temperatures, as well as excess catalyst concentration, resulted in interesting structures, such as nanohorns or nanoflowers, as seen in figure 2d. These structures also generally had considerable amounts of oxygen found by EDS, up to 6 w/o.

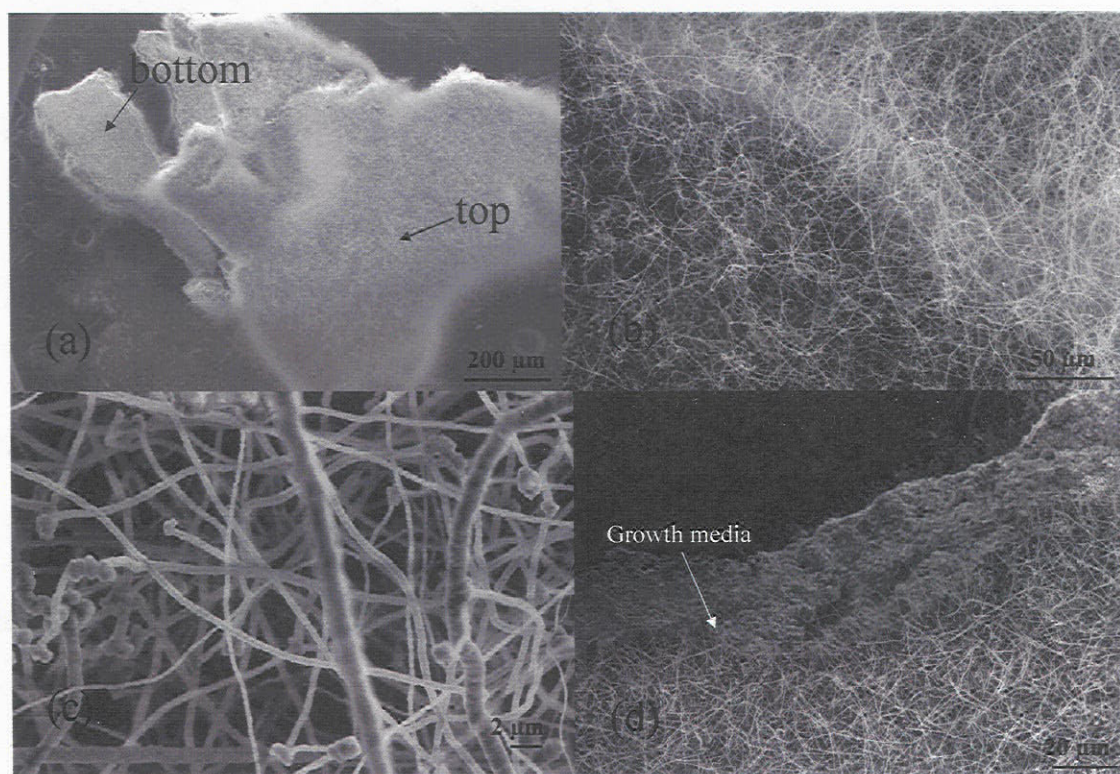


Figure 1 Field emission scanning electron microscope images of BNNT. (a) Typical flake peeled from substrate. (b)(c) Higher magnification photos of typical areas. (d) BNNT growing from media.

Transmission electron microscopy results are shown in Figures 3 and 4. TEM results showed the nanotubes to be nearly stoichiometric BN and a mixture of both straight walled nanotubes, as shown in Figure 3, and the “bamboo” structures, Figure 4. Predominately, the product from this method is multiwalled, commonly composed of 15-30 lattice layers, although this can be affected by processing conditions. Diameters of the

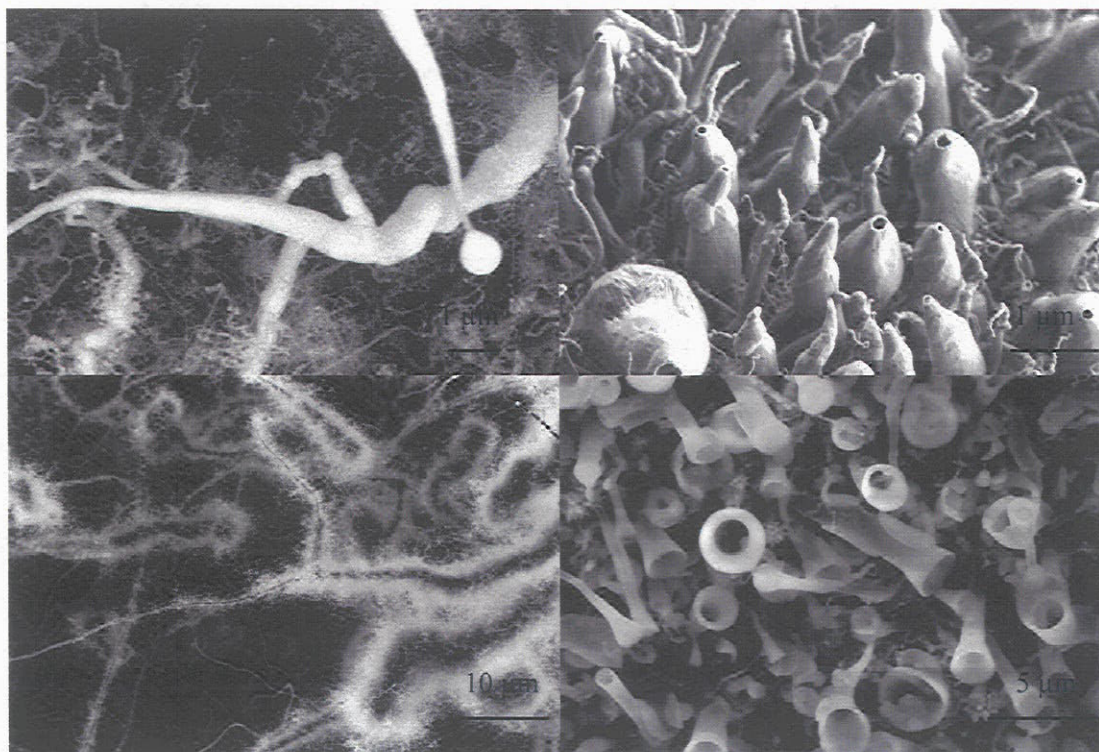


Figure 2. Examples of less typical structures synthesized at processing extremes.

- a) Adjacent extremes in size. b) open ended nanopods c) fine BNNT nucleated on larger tubes d) nanohorns.

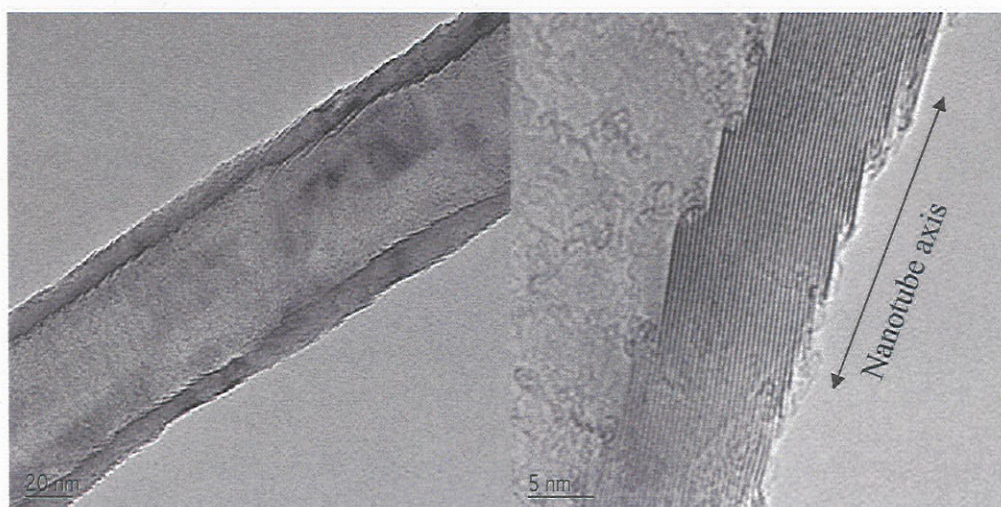


Figure 3 TEM photos of typical straight walled BNNT

multiwalled BNNT were often in the 20-40 nm range, again determined by processing conditions and catalysts concentration. Figure 3 shows the atomic planes within the straight walled nanotubes exhibited lattice fringes at an angle of 12.5° with respect to the

tube axis. This has also been noted elsewhere (5, 13) and may be an indication of rhombohedral stacking order (12). In Figure 4 the typically highly faulted lattice walls of the bamboo structure are evident. These faulted short walls, with their open edge layers, have been suggested to be superior for hydrogen storage (14,15). The structure of the BN layers are analogous to stacked paper cups with potential hydrogen storage sites on the surface and between lattice planes, and also perhaps within the isolated voids. Predominately bamboo structures can be consistently produced by this processing method. Figure 5 shows a region of exclusively bamboo BNNT.

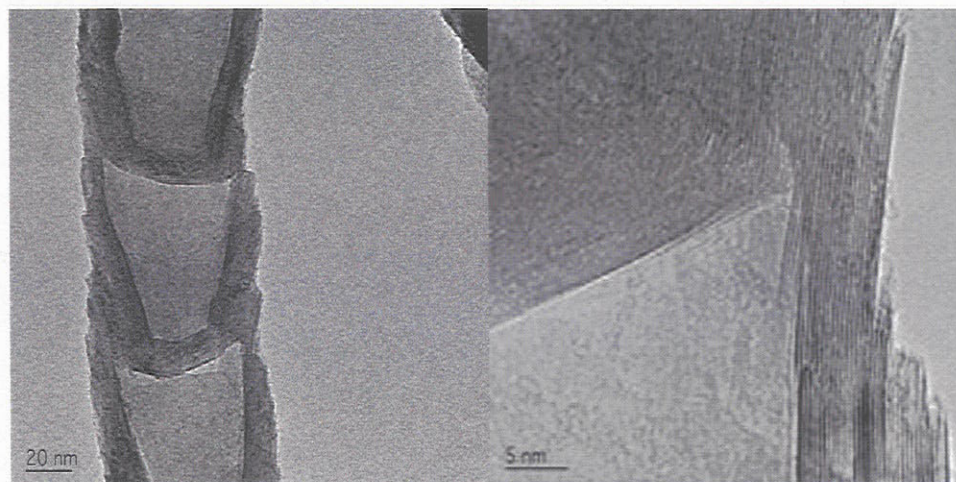


Figure 4 TEM photos of typical bamboo BNNT

The temperature stability of as-produced BN nanotubes was investigated by thermal gravimetric analysis. The results were compared to commercial as-produced carbon nanotubes*. Photos of the as-produced CNT and BNNT materials are shown in Figure 6 as well as those following heating in the TGA. The BNNT structure is clearly intact with the CNT decomposed, leaving behind the extensively oxidized iron catalyst. Figure 7 shows the TGA data in air, confirming that the carbon nanotubes have decomposed by 400 C. However, the BNNT are unaffected by the heat treatment with the exception of some slight weight gain from oxidation above 1000 C.

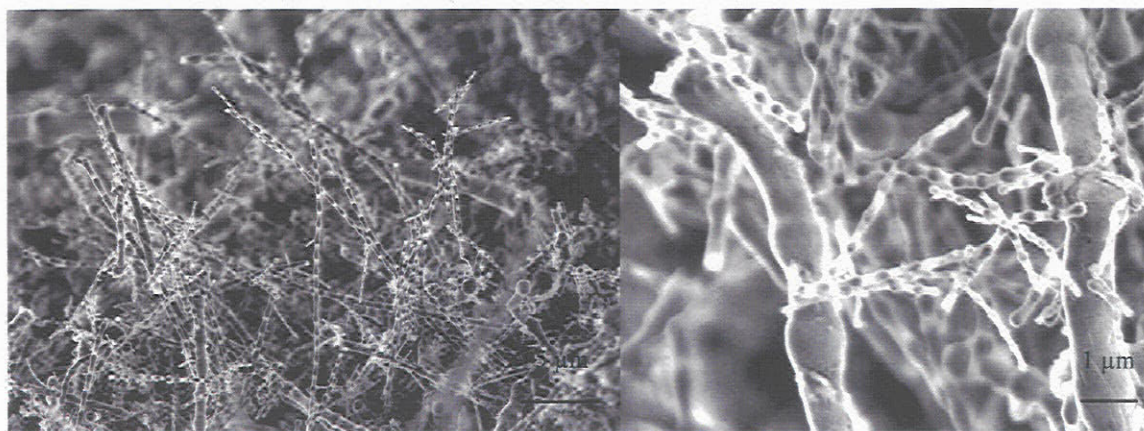


Figure 5. Regions of predominately bamboo nanotubes structures

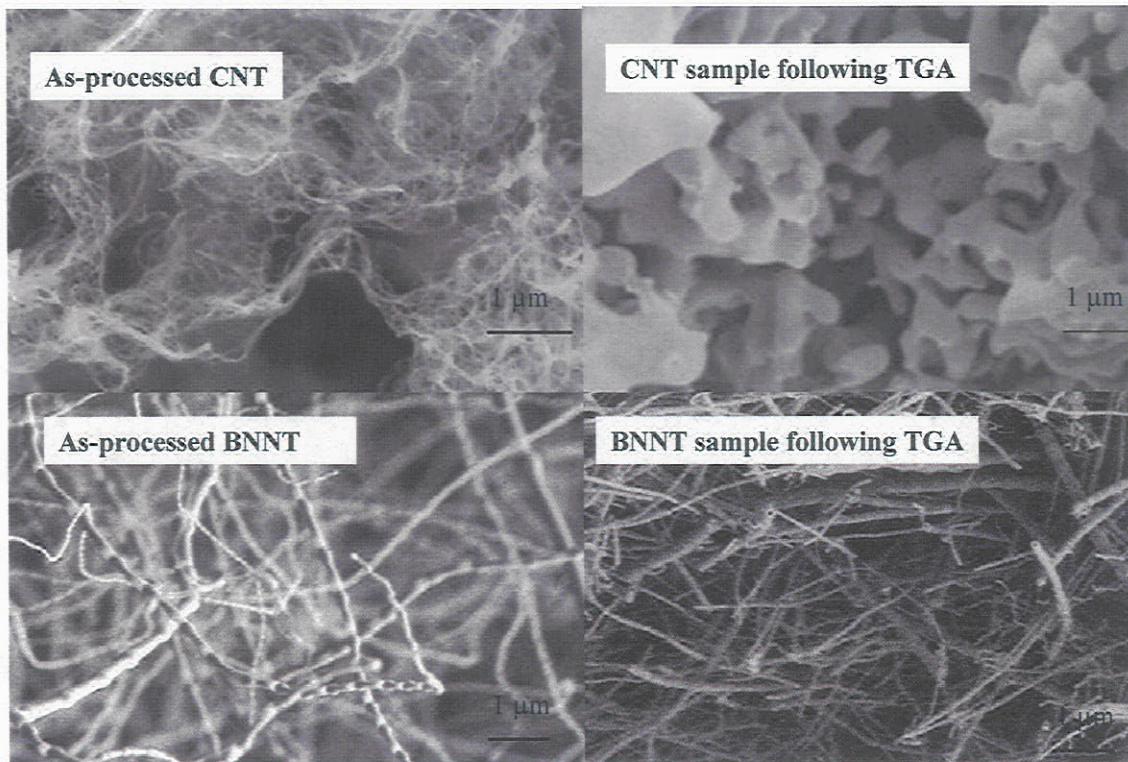


Figure 6. As-processed BNNT and CNT samples were examined before and after exposure in air to 1000 C in a TGA. Photos on the left are as-processed samples. On the right are photos of material remaining following a TGA run to 1000C

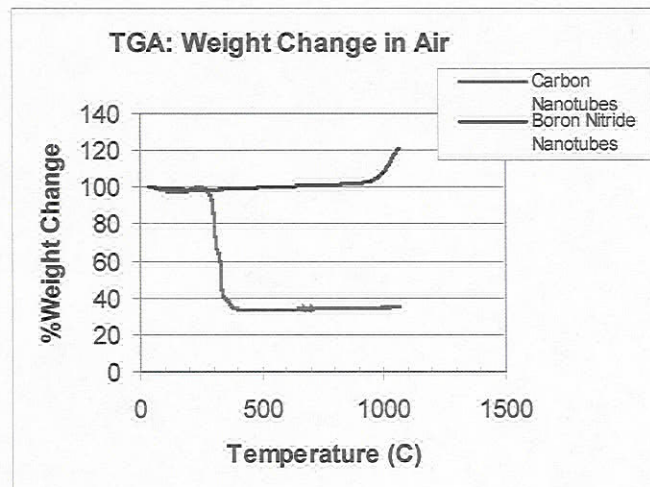


Figure 7. TGA results for BNNT and CNT samples showing the superior stability of BNNT relative to CNT

CONCLUSION

Boron nitride nanotubes were successfully and reproducibly grown by a NASA Glenn Research Center developed process. Currently 1-2 gram batches are being synthesized; however, the process is scaleable to much larger batch sizes. Sufficient amounts are now available so that boron nitride nanotubes are currently being incorporated into composites to provide high strength behavior at high temperature. It is also possible that this material may have many applications for sensors, electronics, piezoelectrics, among other applications of interest to NASA and the technical community.

A preponderance of bamboo structured nanotubes could be achieved by careful additions of catalyst materials and control of processing conditions. These bamboo structures are of interest for hydrogen storage applications. The boron nitride nanotubes were found to be much more stable at high temperature than carbon nanotubes.

ACKNOWLEDGEMENTS

This work was sponsored by the Alternate Fuel Foundation Technologies (AFFT) Subproject of the Low Emissions Alternative Power (LEAP) Project at the NASA Glenn Research Center.

*Carbon Nanotechnologies, Inc., 16200 Park Row, Houston, TX

REFERENCES

- ¹. J. Hurst NASA R&T 2002, NASA TM – 2002-211333.
- ². D. Larkin NASA R&T 2002, NASA TM – 2002-211333
- ³. N.G. Chopra, A. Zettl, "Measurement of the Elastic Modulus of a Multi-wall Boron Nitride Nanotube", Solid State Commun. 105 (1998) 297.
- ⁴. X. Blaise, A. Rubio, S.G. Louie and M.L. Cohen, Europhys. Lett. 28 (1994) 335.
- ⁵. L. Bourgeois, Y. Bando and T. Sato, "Tubes of Rhombohedral Boron Nitride", J. Phys. D: Appl. Phys. 33 (2000) 1902.
- S. M. Nakmanson, A. Cazolari, V. Meunier, J. Bernholc, and M. Buongiorno Nardelli, "Spontaneous Polarization and Piezoelectricity in Boron Nitride Nanotubes", Phy. Rev. B 67, 235406 (2003).
- ⁷. R. Sen, B.C. Satishkumar, A. Govindaraj, K.R. Harikumar, G. Raina, J.P. Zhang, A.K. Cheetham, C.N.R. Rao, "B-C-N, C-N and B-N Nanotubes Produced by the Pyrolysis of Precursor Molecules Over Co Catalysts", Chem. Phys. Lett. 287 (1998) 671.
- ⁸. P. Ma, Y. Bando, and T. Santo, "CVD Synthesis of Boron Nitride Nanotubes Without Metal Catalysts", Chem. Phys. Lett. 337 (2001) 61-64.
- ⁹. N.G. Chopra, R.J. Luyren, K. Cherry, V.H. Cresi, M.L. Cohen, S.G. Louie, A. Zettl, "Boron Nitride Nanotubes", Science, New Series, 269 (1995) 966.
- ¹⁰. D.P. Yu, X.S. Sun, C.S. Lee, I. Bello, S. T. Lee, H. D. Gu, K. M. Leung, G.W. Zhou, Z. F. Dong, Z. Zhang, Appl. Phys. Lett 72 (1998) 1966.

- ¹¹. Y. Chen, L.T. Chadderton, J.S Williams, and J. Fitz Gerald, "Solid State Formation of Carbon and Boron Nitride Nanotubes", Mater. Sci. Forum 343, 63 (2000) 63.
- ¹². Y. Chen, M. Conway, J.S Williams, J. Zou, "Large-Quantity Production of High-Yield Boron Nitride Nanotubes", J. Mater. Res. Vol 17 No.8 (2002) 1896-1899.
- ¹³. R. Ma, Y. Bando, T. Sato and K. Kurashima, " Growth, Morphology, and Structure of Boron Nitride Nanotubes", Chem. Mater. (2001) 13 2965.
- ¹⁴. R. Chen, Y. Bando, H. Zhu, T. Sato, C. Xu, and D. Wu, "Hydrogen Uptake in Boron Nitride Nanotubes at Room Temperature", J. Am. Chem. Soc. 2002, 124 7672.
- ¹⁵. T.Oku, M. Kuno, I. Narita, "Hydrogen Storage in Boron Nitride Nanomaterials Studied by TG/DTA and Cluster Calculations", J. Phys. and Chem. of Solids 65 (2004) 549.